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**BASELINE CHEMISTRY MODEL FOR PLUME  
RADIATION PREDICTIONS**

Edward R. Fisher, et al

Physical Dynamics, Incorporated

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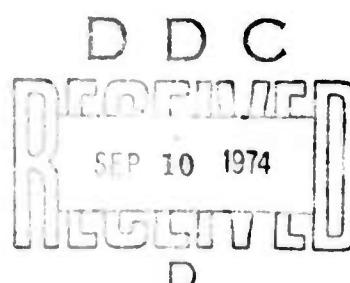
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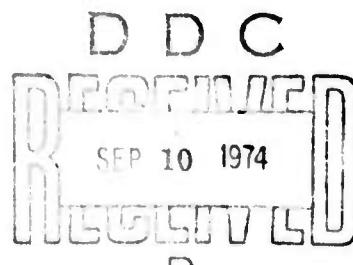
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Four baseline chemistry models which include a detailed reaction mechanism, temperature dependent rate coefficients and radiative properties are presented. The four models include: APOLLO Model for the O/H/OH/H<sub>2</sub>/O<sub>2</sub>/H<sub>2</sub>O system; RELAXATION Model for the O/H/N<sub>2</sub>/CO/H<sub>2</sub>/H<sub>2</sub>O/CO<sub>2</sub> system; HYDROCARBON Model for hydrocarbon fuel afterburning; and AMINE Model for amine/substituted amine afterburning. Preliminary calculations are presented on the RELAXATION and AMINE Models while references are listed for a more thorough discussion.



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## INTRODUCTION

As part of the DARPA Plume Physics Program, extensive modeling calculations have been performed on both field and test environments. These modeling calculations generally involve fluid dynamical, chemical and radiative inputs, each of which may be subject to certain approximations in order to yield a final value for comparison with observation. The purpose of this paper is to outline four chemistry models which can be used for baseline predictions on the IR radiative characteristics of rocket exhaust plumes.

Although these models were initially generated for use in high altitude plume environments where continuum fluid approximations are still valid, the resulting chemistry is also useful to both lower altitude regimes and test environments. The four models developed to date consist of the following:

- (1) APOLLO model
- (2) RELAXATION model
- (3) HYDROCARBON model
- (4) AMINE model .

Each model consists of a chemical mechanism consisting of a sequence of chemical reactions and energy transfer processes with temperature dependent rate coefficients as well as the radiative lifetimes of appropriate species in the IR region of the spectrum. A preliminary attempt to outline a UV model

has been documented elsewhere [Kummier, Fisher, Boynton (1972)].

The rationale behind the development of these baseline chemistry models stems from the desire to provide a common chemistry for direct comparison between different flow field models. In addition, these baseline models provide a state-of-the-art chemistry package to use in making reasonable predictions of plume radiation as well as the radiation observed from rocket test plumes. As new chemical reactions and improved rate coefficient information becomes available, the chemistry models will be updated.

As will become clear in reviewing the chemistry models, many rate coefficients are poorly known. However, the attempt in these models has been to include as much of the important chemistry as is feasible with rate coefficients estimated either from theory or by comparison with other better known rate processes. The output from model calculations can then provide the basis for the design of experiments aimed at quantifying the important chemical rates. This has already been done in several cases, as will be discussed later.

The chemical processes included in these baseline chemistry models must reflect the highly non-equilibrium state of high altitude plumes. Therefore, the following types of chemistry processes have been included in the current models:

Chemi-excitation processes - these are chemical reactions in which the exothermicity of the reaction is either partly or totally deposited directly into an internal energy state of a product molecule. Generally speaking, interest has been focused on product vibrational states since these excited species can directly or indirectly (by transferring the vibrational energy to another species or mode) contribute to observed IR radiation levels. An example of this type of process is



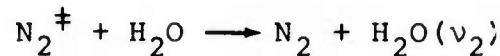
where  $\text{H}_2\text{O}^+$  represents a vibrationally excited molecule. Sufficient reaction energy exists in this process to excite either the stretching or bending modes. As a result of interest generated in this and related processes, experiments have been performed on the quantum yield of these reactions [Trainor (1973)].

Relaxation processes - these are energy transfer processes in which vibrational energy is exchanged with translational or rotational energy (VT) in a collision, or vibrational energy is exchanged directly between vibrational modes (VV). As an example of the former case (VT), the process



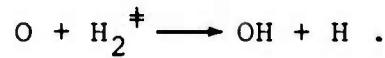
is thought to be important in the mixing layer of high altitude plumes. Since vibrational relaxation processes involving atomic species are known to be important in cases where direct experiment has been performed, plume radiation by O atoms is believed to be of major importance in the mixing layer of high altitude plumes. The rates for several of these O atom relaxation processes have

been measured as part of the Plume Physics Program and the results are included in the models. As an example of a VV process



may contribute to the excitation of  $\text{H}_2\text{O}$  by atmospheric  $\text{N}_2$  which is vibrational excited in passing through the air shock prior to entering the mixing layer. Non resonance in vibrational energy in VV processes is supplied or absorbed by the local kinetic and rotational energy dependin~ on the direction of the reaction. For both VT and VV processes, a significant amount of rate coefficient information was obtained from the results of past laser studies.

Excited state processes - these are chemical reactions in which the reactants are in excited internal energy states. By detailed balance arguments based on chemi-excitation reactions, excited state processes are expected to be important in the plume environment. A particularly significant excited state process is



This reaction between atmospheric O atoms and vibrationally excited  $\text{H}_2$  may be the source reaction for the vibrationally excited OH observed in APOLLO at high altitudes. This reaction also generates ground state OH which can subsequently react with more  $\text{H}_2$  to generate  $\text{H}_2\text{O}$  as outlined under chemi-excitation reactions above. The ground state reaction



has been extensively measured and is well known over the temperature range of interest in plume modeling. The activation energy of 9.5 kcal/mole represents a substantial barrier to the generation of OH in low temperature environments such as rocket plumes. However, if the  $H_2(v=1)$  state, with an energy of 13 kcal/mole above  $H_2(v=0)$ , can provide this activation energy then the excited state reaction might proceed with near gas kinetic rate providing an important production reaction for OH. Unfortunately, this excited state reaction is not easily amenable to experimental determination, but current theoretical efforts underway at Wayne State University in collaboration with Brookhaven National Laboratory may permit evaluation of the rate and energy flow in this excited state reaction.

Fuel afterburning reactions - these are generally highly exothermic chemical reactions between atmospheric O atoms and partially reacted or unreacted fuel fragments which find their way into the plume gas through boundary layer flow, peripheral flows (turbine and exhaustuator flows), or incomplete combustion processes. Although the fraction of fuel fragments in the plume flow is generally small (of order 1%) the rate and energetics of fuel species make even this small amount significant in an overall radiation energy balance. An example of a fuel afterburning reaction is the the reaction



which proceeds very rapidly with an exothermicity of about 90 kcal/mole. As discussed in a later section of

this report, the H<sub>2</sub>O molecule is likely to be highly vibrationally excited and this provides a substantial source of IR radiation.

#### DISCUSSION OF MODELS

It is not the intention of this paper to provide an exhaustive review of the four plume chemistry models, but to indicate their availability, to provide some measure of their reliability, and to present some preliminary calculations performed using these models. Although reports have been prepared detailing the four models [Fisher (1973a); Kummler, Fisher, Boynton (1972, 1973)], a summary tabulating the reactions, rate coefficients and references are given in Appendix I.

#### Relaxation Model

In this section, we will present a calculation using the RELAXATION model on a TITAN core streamline. This calculation will indicate the detail included in the model as well as the methodology of reducing the size of the chemistry package for specific applications. A report detailing these TITAN core calculations is being prepared [Fisher (1973b)].

In Figure 1, the effective vibrational temperatures of important modes on an outermost TITAN core streamline are shown.

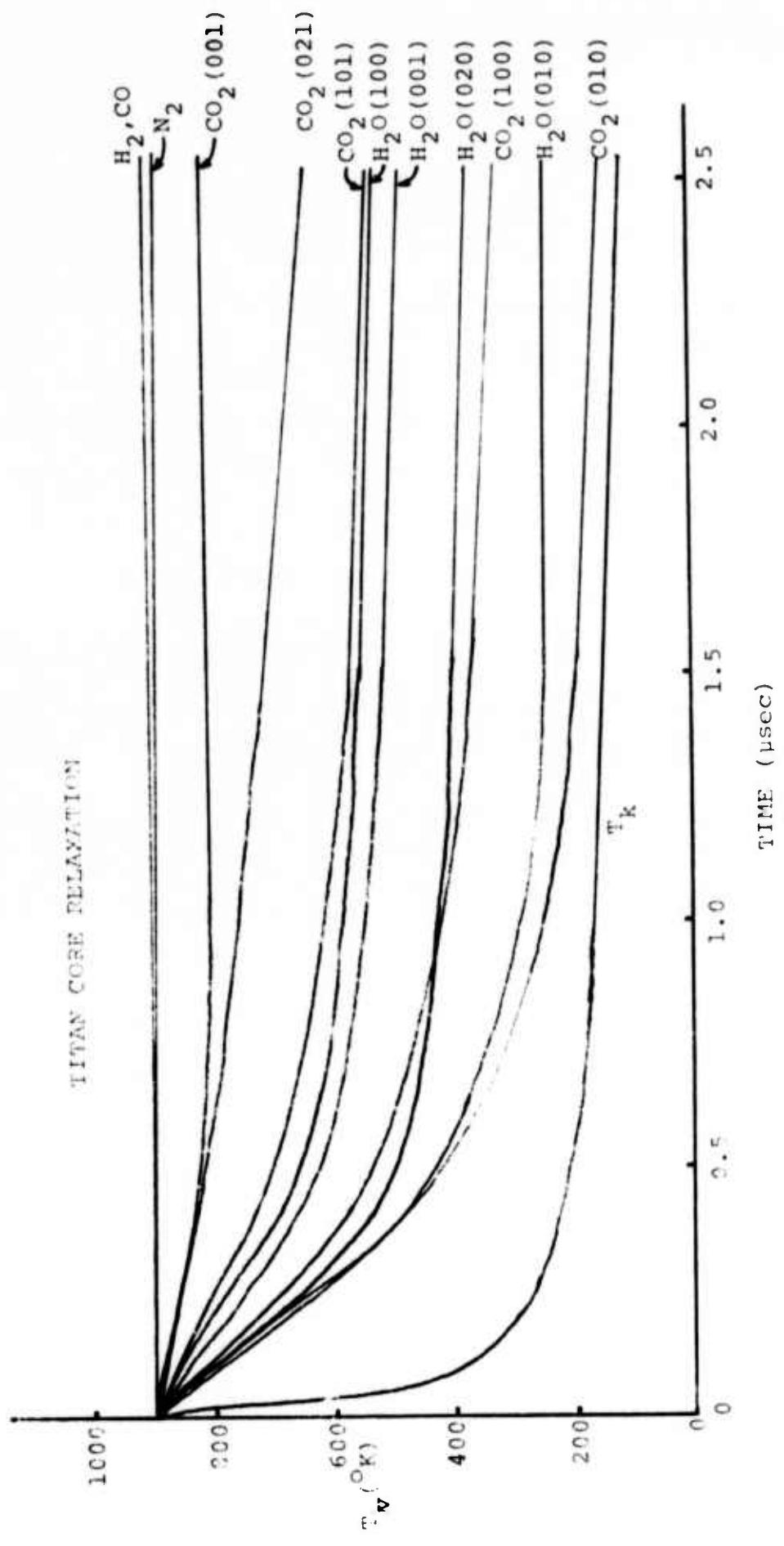


FIGURE 1. Vibrational temperatures in an "outermost" streamline of a TITAN core flow calculated using the RELAXATION Model [Fisher (1973b)].

The calculation was done using a Runge-Kutta-Merson integration procedure with algebraic subroutine for treating the chemistry which is in a quasi steady state. These quasi steady state reactions generally force the system of chemical reactions into a "stiff" condition which greatly increases integration time for standard integrations packages. The algebraic subroutine provides a mechanism to bypass this complication as has been extensively discussed before [Fisher, Kummier (1968)].

The general features that emerge from this calculation are that the diatomic molecules are vibrationally frozen at rear exit conditions; the bending modes of CO<sub>2</sub> and H<sub>2</sub>O are nearly in equilibrium with the translational temperature while the stretching modes are partially frozen depending on the extent of VV coupling to the diatomic species. Due to the rapid VV transfer with N<sub>2</sub>(v=1), CO<sub>2</sub>(001) is rather vibrationally hot along this streamline. The modes of CO<sub>2</sub> which depend on CO<sub>2</sub>(001) as a source, i.e., CO<sub>2</sub>(021) and CO<sub>2</sub>(101) are also rather vibrationally hot but reflect the fact that the bending modes of CO<sub>2</sub> are rather vibrationally cold.

The RELAXATION model maintains the Fermi resonance between CO<sub>2</sub>(100) and CO<sub>2</sub>(020) as a VT process with nearly gas kinetic efficiency independent of the collision species, while the H<sub>2</sub>O(100) and (001) modes are assumed to be in quasi equi-

librium at the local kinetic temperature. This latter assumption stems from the closeness in energy resonance between these modes as well as the sparcity of data regarding the relaxation of higher vibrational levels in H<sub>2</sub>O.

The code used in these calculations also provides a "picture" of the important rate processes involving each excited species. This output, called HISTORY, is provided at arbitrary time intervals in the calculation and permits evaluation of the significant reactions both supplying and destroying any particular level. Two such reaction profiles are shown in Tables I and II for two times. Note that the rate coefficients are not generally the same for the two tables reflecting the change in temperature while the difference in rates reflect not only the change in excited species density due to relaxation but also due to pressure. Both the translational temperature and pressure are printed at the top of the respective tables. By using these rate profiles, it is anticipated that the number of relaxation processes can be reduced for subsequent calculations in similar environments.

Since the hydrocarbon afterburning model has been discussed previously [Kummeler, Fisher, Boynton (1972)], the amine afterburning model will be more extensively detailed here. Further background information can be obtained in report form [Kummeler, Fisher, Boynton (1973)].

TABLE I

Chemical reactions, rate coefficients and separate rates at beginning of relaxation calculation in TITAN core flow as obtained from subroutine HISTORY [Fisher (1973b)].

NO.	TIME = N.F SEC	REACTIONS	PRES = 1.512E-01 ATM	TEMP = 898.00 K	CONSTANT		RATE
					C	H	
1.	H2*	+ H	= H2	+ H	6.731E-12	0.0	
2.	H2	+ H	= H2*	+ H	8.343E-15	0.0	
3.	H2*	+ C	= H2	+ C	8.990E-12	0.0	
4.	H2	+ C	= H2*	+ C	1.114E-14	0.0	
5.	H2*	+ H2	= H2	+ H2	8.271E-14	7.085E 18	
6.	H2	+ H2	= H2*	+ H2	1.025E-16	6.920E 18	
7.	H2*	+ H2 <sup>0</sup>	= H2	+ H2 <sup>0</sup>	9.271E-14	1.040E 19	
8.	H2	+ H2 <sup>0</sup>	= H2*	+ H2 <sup>0</sup>	1.025E-16	1.015E 19	
9.	N2*	+ H	= N2	+ H	2.889E-18	0.0	
10.	N2	+ H	= N2*	+ H	6.791E-20	0.0	
11.	N2*	+ C	= N2	+ C	1.106E-14	0.0	
12.	N2	+ C	= N2*	+ C	2.598E-16	0.0	
13.	N2*	+ H2	= N2	+ H2	1.612E-15	3.665E 18	
14.	N2	+ H2	= N2*	+ H2	3.785E-17	3.617E 18	
15.	N2*	+ H2 <sup>0</sup>	= N2	+ H2 <sup>0</sup>	1.610E-15	5.378E 18	
16.	N2	+ H2 <sup>0</sup>	= N2*	+ H2 <sup>0</sup>	3.785E-17	5.307E 18	
17.	OH*	+ H	= OH	+ H	3.070E-11	0.0	
18.	OH	+ H	= OH*	+ H	9.673E-14	0.0	
19.	OH*	+ O	= OH*	+ O	3.070E-11	0.0	
20.	OH	+ O	= CH*	+ O	9.603E-14	0.0	
21.	OH*	+ H2	= OH	+ H2	1.070E-11	1.028E 14	
22.	OH	+ H2	= OH*	+ H2	3.201E-14	1.008E 14	
23.	OH*	+ H2 <sup>0</sup>	= CH	+ H2 <sup>0</sup>	3.000E-12	4.526E 13	
24.	OH	+ H2 <sup>0</sup>	= OH*	+ H2 <sup>0</sup>	9.603E-15	4.436E 13	
25.	H2O	+ C1 <sup>0</sup>	H	= H2O CCO + H	2.000E-10	0.0	
26.	H2O	+ CO <sup>0</sup>	H	= H2O CCO + H	1.536E-11	0.0	
27.	H2O	+ CO <sup>0</sup>	O	= H2O CCO + O	1.020E-11	0.0	
28.	H2O	+ CO <sup>0</sup>	O	= H2O CCO + O	7.679E-13	0.0	
29.	H2O	+ CO <sup>0</sup>	H2	= H2O CCO + H2	1.000E-11	7.071E 22	
30.	H2O	+ CO <sup>0</sup>	H2	= H2O CCO + H2	7.679E-13	7.008E 22	
31.	H2O	+ CO <sup>0</sup>	H2 <sup>0</sup>	= H2O CCO + H2 <sup>0</sup>	1.000E-11	1.038E 23	
32.	H2O	+ CO <sup>0</sup>	H2 <sup>0</sup>	= H2O CCO + H2 <sup>0</sup>	7.679E-13	1.028E 23	
33.	H2O	+ CO <sup>0</sup>	H	= H2O CCO + H	1.000E-11	0.0	
34.	H2O	+ CO <sup>0</sup>	H	= H2O CCO + H	2.372E-14	0.0	
35.	H2O	+ CO <sup>0</sup>	O	= H2O CCO + O	1.000E-11	0.0	
36.	H2O	+ CO <sup>0</sup>	O	= H2O CCO + O	2.372E-14	0.0	
37.	H2O	+ CO <sup>0</sup>	H2	= H2O CCO + H2	2.000E-13	4.423E 19	

TABLE I (cont'd)

38.	H2O	CC1+ H2	= H2O	CC1+ H2	4. 330E-19
39.	H2O	CC1+ H2O	= H2O	CC0+ H2O	3. 245E-20
40.	H2O	CC1+ H2O	= H2O	CC1+ H2O	3. 177E-20
41.	H2O	CC1+ H	= H2O	CC0E-11	0. 0
42.	H2O	CC1+ H	= H2O	CC0E-15	2. 372E-15
43.	H2O	CC1+ O	= H2O	CC0E-11	3. 781E-12
44.	H2O	CC1+ O	= H2O	CC0E-11	1. 660E-12
45.	H2O	CC1+ H2	= H2O	CC0E-11	1. 0C0E-11
46.	H2O	CC1+ H2	= H2O	CC1+ H2	3. 781E-12
47.	H2O	CC1+ H2O	= H2O	CC0E-11	1. 660E-11
48.	H2O	CC1+ H2O	= H2O	CC1+ H2O	3. 781E-12
49.	CO*	CC1+ H	= CO*	CC1+ H	2. 889E-17
50.	CO*	CC1+ H	= CO*	CC1+ H	2. 344E-21
51.	CO*	CC1+ O	= CO*	CC1+ O	2. 12E-21
52.	CO*	CC1+ O	= CO*	CC1+ O	2. 04E-21
53.	CO*	CC1+ H2	= CO*	CC1+ H2	3. 245E-21
54.	CO*	CC1+ H2	= CO*	CC1+ H2	3. 795E-19
55.	CO*	CC1+ H2O	= CO*	CC1+ H2O	5. 636E-19
56.	CO*	CC1+ H2O	= CO*	CC1+ H2O	5. 568E-19
57.	CO2	CC10+ H	= CO2	CC9+ H	0. 0
58.	CO2	CC9+ H	= CO2	CC9+ H	0. 0
59.	CO2	CC10+ O	= CO2	CC9+ O	0. 0
60.	CO2	CC9+ O	= CO2	CC10+ O	0. 0
61.	CO2	CC10+ H2	= CO2	CC9+ H2	0. 0
62.	CO2	CC9+ H2	= CO2	CC10+ H2	0. 0
63.	CO2	CC10+ H2O	= CO2	CC9+ H2O	0. 0
64.	CO2	CC9+ H2O	= CO2	CC10+ H2O	0. 0
65.	CO2	CC10+ CO2	= CO2	CC9+ CO2	0. 0
66.	CO2	CC9+ CO2	= CO2	CC10+ CO2	0. 0
67.	CO2	CC10+ H	= CO2	CC9+ H	0. 0
68.	CO2	CC9+ H	= CO2	CC10+ H	0. 0
69.	CO2	CC10+ O	= CO2	CC9+ O	0. 0
70.	CO2	CC9+ O	= CO2	CC10+ O	1. 086E-14
71.	CO2	CC10+ H2	= CO2	CC9+ H2	3. 947E-14
72.	CO2	CC9+ H2	= CO2	CC10+ H2	9. 072E-16
73.	CO2	CC10+ H2O	= CO2	CC9+ H2O	3. 947E-14
74.	CO2	CC9+ H2O	= CO2	CC10+ H2O	9. 072E-16
75.	CO2	CC10+ H	= CO2	CC9+ H	5. 084E-14
76.	CO2	CC9+ H	= CO2	CC10+ H	2. 669E-14
77.	CO2	CC10+ O	= CO2	CC9+ O	2. 892E-13
78.	CO2	CC9+ O	= CO2	CC10+ O	1. 479E-13

TABLE I (cont'd)

TABLE I (cont'd)

TABLE II  
Chemical reactions, rate coefficients and individual rates at  $1.62\mu$  sec in TITAN core  
flow as obtained from subroutine HISTORY [Fisher (1973b)].

NO.	TIME = $1.62 \times 10^{-6}$ SEC			PRES = $1.861 \times 10^{-14}$ ATM			KINETICS OF THE REACTIONS			TEMP = $140.26$ K			RATE
1.	H2*	+ H	= H2*	+ H	+ H								$1.480E-15$
2.	H2	+ H	= H2*	+ H	+ H								$3.628E-34$
3.	H2*	+ C	= H2*	+ C	+ H2								$3.553E-12$
4.	H2	+ C	= H2*	+ C	+ H2								$8.71CE-31$
5.	H2*	+ H2	= H2*	+ H2	+ H2								$3.593E-19$
6.	H2	+ H2	= H2*	+ H2	+ H2								$8.89E-38$
7.	H2*	+ H2 <sup>r</sup>	= H2*	+ H2 <sup>r</sup>	+ H2 <sup>r</sup>								$3.593E-19$
8.	H2	+ H2 <sup>r</sup>	= H2*	+ H2 <sup>r</sup>	+ H2 <sup>r</sup>								$8.89E-38$
9.	N2*	+ H	= N2*	+ H	+ H								$8.725E-13$
10.	N2	+ H	= N2*	+ H	+ H								$2.735E-26$
11.	N2*	+ C	= N2*	+ C	+ O								$1.019E-36$
12.	N2	+ C	= N2*	+ O	+ O								$1.433E-15$
13.	N2*	+ H2	= N2*	+ H2	+ H2								$5.340E-26$
14.	N2	+ H2	= N2*	+ H2	+ H2								$7.594E-22$
15.	N2*	+ H20	= N2*	+ H20	+ H20								$2.829E-32$
16.	N2	+ H20	= N2*	+ H20	+ H20								$7.594E-22$
17.	OH*	+ H	= OH	+ H	+ H								$2.829E-32$
18.	OH	+ H	= CH*	+ H	+ H								$3.450E-11$
19.	OH*	+ O	= CH	+ O	+ O								$3.197E-27$
20.	OH	+ O	= OH*	+ O	+ O								$3.197E-27$
21.	OH*	+ H2	= OH	+ H2	+ H2								$1.010E-11$
22.	OH	+ H2	= OH*	+ H2	+ H2								$1.010E-11$
23.	OH*	+ H20	= CH	+ H20	+ H20								$1.010E-12$
24.	OH	+ H20	= CH*	+ H20	+ H20								$1.010E-12$
25.	H2O	+ H	= H2O	+ H	+ H								$2.045E-10$
26.	H2O	+ H	= H2O	+ H	+ H								$1.459E-17$
27.	H2O	+ O	= H2O	+ O	+ O								$1.002E-11$
28.	H2O	+ O	= H2O	+ O	+ O								$7.296E-19$
29.	H2O	+ H2	= H2O	+ H2	+ H2								$1.002E-11$
30.	H2O	+ H2	= H2O	+ H2	+ H2								$7.296E-19$
31.	H2O	+ H20	= H2O	+ H20	+ H20								$1.000E-11$
32.	H2O	+ H20	= H2O	+ H20	+ H20								$7.296E-19$
33.	H2O	+ H	= H2O	+ H	+ H								$1.000E-11$
34.	H2O	+ H	= H2O	+ H	+ H								$1.565E-28$
35.	H2O	+ O	= H2O	+ O	+ O								$1.565E-28$
36.	H2O	+ O	= H2O	+ O	+ O								$1.565E-28$
37.	H2O	+ H2	= H2O	+ H2	+ H2								$2.002E-13$

TABLE II (cont'd)

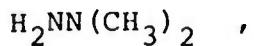
TABLE II (cont'd)

79.	C02	091+	H2		6.571E-15	2.833E-18
80.	C02	030+	H2		8.966E-17	1.406E-14
81.	C02	011+	H20		9.852E-14	6.234E-19
82.	C02	030+	H20		1.344E-15	3.094E-15
83.	C02	011+	C02		1.513E-15	3.018E-17
84.	C02	030+	C02		2.065E-17	1.498E-13
85.	C02	011+	CO		1.135E-15	2.264E-17
86.	C02	030+	CO		1.548E-17	1.123E-13
87.	C02	011+	N2		1.135E-15	7.088E-17
88.	C02	030+	N2		1.548E-17	3.518E-13
89.	H2*		H20	000	4.684E-15	5.655E-17
90.	H2*		H20	001	7.337E-17	1.759E-14
91.	H2*		OH	*	1.503E-12	3.846E-12
92.	H2*		OH	*	2.380E-15	6.467E-08
93.	N2*		H20	010	3.000E-13	6.306E-16
94.	N2*		H20	001	5.211E-14	1.770E-17
95.	N2*		H20	000	4.194F-16	1.313E-18
96.	N2		H20	010	2.141E-19	1.957E-12
97.	H20	010	H20	010	1.184E-11	7.535E-15
98.	H20	020	H20	000	7.957E-12	1.207E-19
99.	C02	011+	H20	000	1.000E-13	6.134E-19
100.	C02	010+	H20	010	4.581E-14	5.671E-14
101.	N2*		C02	000	1.154E-12	1.346E-21
102.	N2		C02	001	1.398E-12	8.274E-20
103.	N2*		CO	*	5.54E-15	4.828E-18
104.	N2		CO*	*	7.330E-16	9.849E-17
105.	C02	001+	CO	*	4.750E-14	8.893E-18
106.	C02	000+	CO*	*	5.688E-15	2.294E-18
107.	C02	011+	H20	000	2.369E-12	7.698E-18
108.	C02	000+	H20	001	3.569E-12	3.639E-18
109.	C02	021+	H20	000	2.369E-12	6.143E-19
110.	C02	000+	H20	001	1.075E-11	1.096E-19
111.	C02	101+	C02	000	2.369E-10	2.230E-20
112.	C02	100+	C02	001	2.959E-10	2.184E-20
113.	C02	020+	C02	000	4.737E-12	3.700E-19
114.	C02	010+	C02	000	7.856E-12	2.385E-18
115.	H20	020+	H		4.000E-10	0.0

TABLE II (cont'd)

### Chemical Models: Substituted Hydrazine

The chemistry of RHNNR'R" compounds is quite different from the hydrogen and hydrocarbon chemistry reviewed previously [Kummller, Fisher, Boynton (1972)] because of the characteristic strong NN bonding. In addition, the different chemical behavior of unsymmetrical dimethyl hydrazine (UDMH),



and hydrazine or monomethyl hydrazine (MMH),

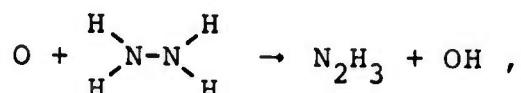


precludes some of the simplicity of the generalizations inherent in the lumped parameter approach to the hydrocarbon oxidation. Major radiating steps in the plume appear to be associated with the initial attack of O atoms on the fuel-like species, rather than the secondary reactions of products of the initial attack as in hydrocarbon oxidation.

Oxygen atom attack on hydrazine has been studied using high intensity crossed molecular beams [Gehring, et al (1970), Foner and Hudson (1970)]. The products of the reaction have been found to be  $\text{N}_2\text{H}_2 + \text{H}_2\text{O}$ , via the elementary reaction:

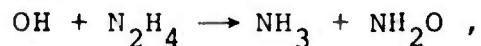


This reaction is highly exothermic (90 kcal) and forms a completely new water molecule by simultaneously abstracting two hydrogen atoms. The expected (from, for example, the analogous O attack on ethylene) atom transfer reaction,



which is 26 kcal exothermic, is about 1/25 as probable [Foner and Hudson (1970)]. The reaction of O + UDMH can only produce OH.

Once significant quantities of OH become available through the latter reactions, additional processes are possible. Again, high intensity molecular beams [Gehring, et al (1970)] have been used to identify the products of the reaction:



which is the key reaction in severing the N-N bond.

The likely mechanism for oxidation of substituted hydrazine compounds is illustrated schematically in Figure 2. The reaction rate constants for the principal reactions are given in Table III. A more complete literature review of pertinent reactions has been given by Kummeler, Fisher and Boynton (1973), while a summary of the Amine model is given in Appendix I.

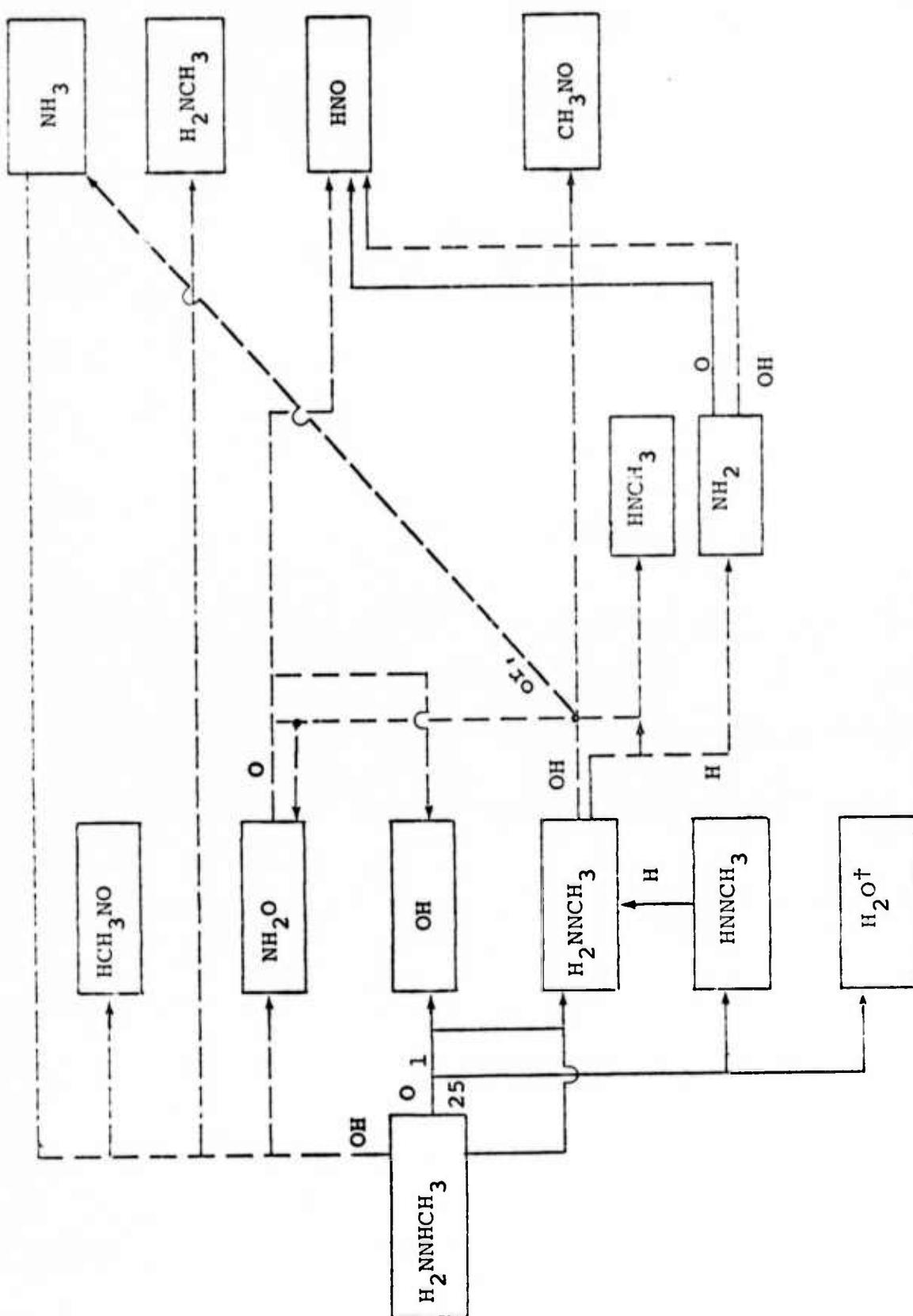


FIGURE 2. Simplified O atom oxidation mechanism for UDNH ( $\text{UDNH}$  and  $\text{N}_2\text{H}_4$  are similar) illustrating the stable species which can form in this system as intermediates. The dotted lines represent reactions which are probable, but which have not yet been experimentally observed.

TABLE III  
INFRARED HYDRAZINE MODEL A

FUEL CHEMI-EXCITATION REACTIONS

<u>Reaction</u>	<u>Assumed Products*</u>	<u>Forward Rate Constant cc/sec</u>	<u>Reaction Energy kcal/gmole</u>	<u>Reference</u>
$O + MMH \rightarrow NH_2CH_3 + H_2O(001)$				
	(100)	$2 \times 10^{-11}$	-102	Foner and Hudson (1970)
	$H_2O(020)$			
	(010)			
$O + N_2H_4 \rightarrow N_2H_2 + H_2O(001)$				
	(100)	$1.8 \times 10^{-11}$	-90	Gehring, et al (1969)
	$H_2O(020)$			
	(010)			
$O + UDMH \rightarrow HN_2(CH_3)_2 + OH$		$1 \times 10^{-12}$	-25	Analogy
$OH + N_2H_4 \rightarrow NH_3 + NH_2O$		$2 \times 10^{-11}$	?	Gehring, et al (1970)

\* This puts about 40% of the reaction energy into the stretching modes of product  $H_2O$ . (For purposes of computational convenience, we have treated a molecule excited to the second level as two singly-excited molecules; the quenching is thus somewhat more efficient than it should be.)

The salient features of Figure 2 have been examined experimentally in the Wayne State University discharge flow system. Comparative results for  $O + N_2H_4$  chemiluminescence are presented in Figure 3. The reaction of  $H + NO_2$  produces OH, but is not sufficiently exothermic to produce more than  $v=2$  in the product molecule. Hence, the OH fundamental between  $2.7\mu$  and  $3.0\mu$  is broader than the overtone at  $1.5\mu$ . (The instrumental response has not been taken out of Figure 2, so that the overtone appears larger than the fundamental. Calibration with the  $NO + O$  glow reverses this effect and gives excellent agreement with observed values of the overtone to fundamental intensity ratio.) For the reaction of  $O + C_2H_4$  the overtone shows hot bands consistent with the greater available energy. The CO overtone at  $2.3\mu$  also appears and the intensity ratio of the overtone to fundamental ratio under these conditions indicates that some  $H_2O(100)$  and  $H_2O(001)$  radiation may be present. The reaction of  $O + N_2H_4$  exhibits a much broader peak at  $2.7\mu$  indicative of  $H_2O(100)$  and (001) radiation and a band at  $1.9\mu$  also indicative of  $H_2O$  emission is present. The emission of these systems will be analyzed in detail elsewhere.

In order to assess the potential magnitude of the resulting infrared emission, we have taken the mechanism of Figure 2 and reduced it to the simplest form consistent with the production and loss of vibrationally excited  $H_2O$ . We have also

included a number of VT and VV excitation and de-excitation reactions for  $H_2O$  in order to have a basis for comparing calculations with and without chemi-excitation and to provide for quenching of excited species produced by reaction. The mechanism is presented in Appendix I; rate data for the  $H_2O$  VV and VT processes are the same as we have used in calculations on the Apollo system [Boynton (1973)] and follow the recommendations of the Plume Chemistry Workshop held at Physical Dynamics, Berkeley, in January 1973 [Fisher (1973a)].

The rate equations for the above mechanism were integrated through a flow field simulating the mixing layer of a Titan II exhaust plume at 120 km. Details of the flow field calculation will be presented in a separate report, but a brief outline is presented here. The exit plane conditions are taken from an unpublished nozzle flow calculation by D. Thomas (Aerospace Corp.) who included finite-rate chemistry and film cooling effects. External flow calculations were performed with the MULTITUBE and BOW codes [Boynton (1971)]. Unburned fuel concentrations of 5% in the film cooling layer and 1% in the interior exhaust gases were assumed; reactions of  $N_2H_4$  and UDMH with O were included in the flow field calculation, so that depletion of these species would be properly accounted for in a subsequent (overlay) chemistry calculation.

Figure 3. A comparison of the infrared emission spectra for the reactions  $O + N_2H_4$ ,  $O + C_2H_4$  and  $H + NO_2$ . Concentrations of O and H were approximately  $10\mu$  and the concentrations of  $N_2H_4$ ,  $C_2H_4$  and  $NO_2$  were approximately  $2\mu$ ,  $10\mu$  and  $4.5\mu$  respectively. All spectra were taken at a contact time of less than 2 msec. Both O and H were diluted in a stream consisting primarily of He.

$H + NO_2 \rightarrow$ ;  $2000\mu$  slits,  $50\mu$  vFS,  $100\mu$  FS,  $\tau = 10$ , 1 RPM,  $\frac{5 \text{ min}}{\text{in}}$ ,  
 $800\mu$  He,  $200\mu$   $H_2$ ,  $5\mu$   $NO_2$ ,  $5\mu$  H, 1st window.

$O + C_2H_4 \rightarrow$ ;  $1000\mu$  slits,  $50\mu$  vFS,  $100\mu$  FS,  $\tau = 10$ , 1 RPM,  $\frac{5 \text{ min}}{\text{in}}$ ,  
 $10\mu$   $C_2H_4$ ,  $800\mu$  He,  $200\mu$   $O_2$ , 1st window.

$O + N_2H_4 \rightarrow$ ;  $2000\mu$  slits,  $20\mu$  vFS,  $100\mu$  FS,  $\tau = 3, 4$  RPM,  $\frac{2 \text{ min}}{\text{in}}$ ,  
 $2\mu$   $N_2H_4$ ,  $900\mu$  He,  $90\mu$   $O_2$ ,  $11\mu$  O, 1st window.

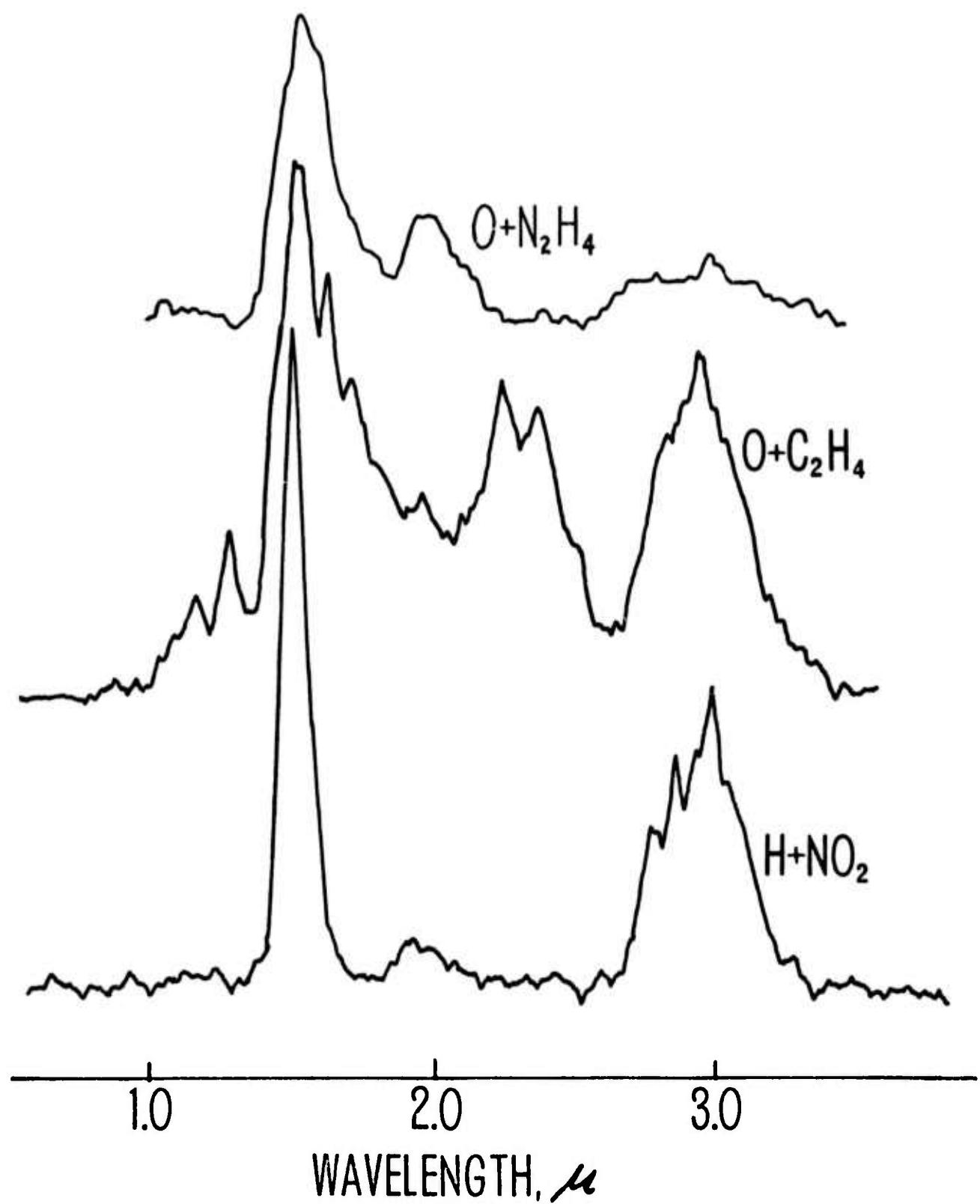


FIGURE 3.

Results of these exploratory calculations are shown in Figure 4. We show cumulative radiant intensity as a function of distance behind the vehicle for the sum of the  $H_2O$  (100) and (001) bands and the OH band (which is negligible in this calculation because important formation mechanisms such as  $H_2 + O \rightarrow OH + H$  have not been included). The lower curve is for the  $H_2O$  excitation processes alone, and the upper curve includes the effects of the simplified chemi-excitation mechanism.

With the assumption of product energy distribution together with those about initial fuel concentrations, there is a substantial difference in calculated radiant intensity with and without chemiluminescent reaction.

These calculations may overestimate the contribution of chemiluminescence to the plume signature for any or all of the following reasons:

- 1) The exhaust-gas concentrations of  $N_2H_4$  and UDMH may be too high. In that connection, note that  $N_2H_4$  (the major reacting species in this system) is a good mono-propellant and decomposes spontaneously at elevated temperatures to give less reactive  $NH_3$ ,  $N_2$ , and  $H_2$ . The amount of external reaction may depend on the extent of such decomposition as well as the overall unburned fuel level. This should not be the case with MMH, which is more stable.

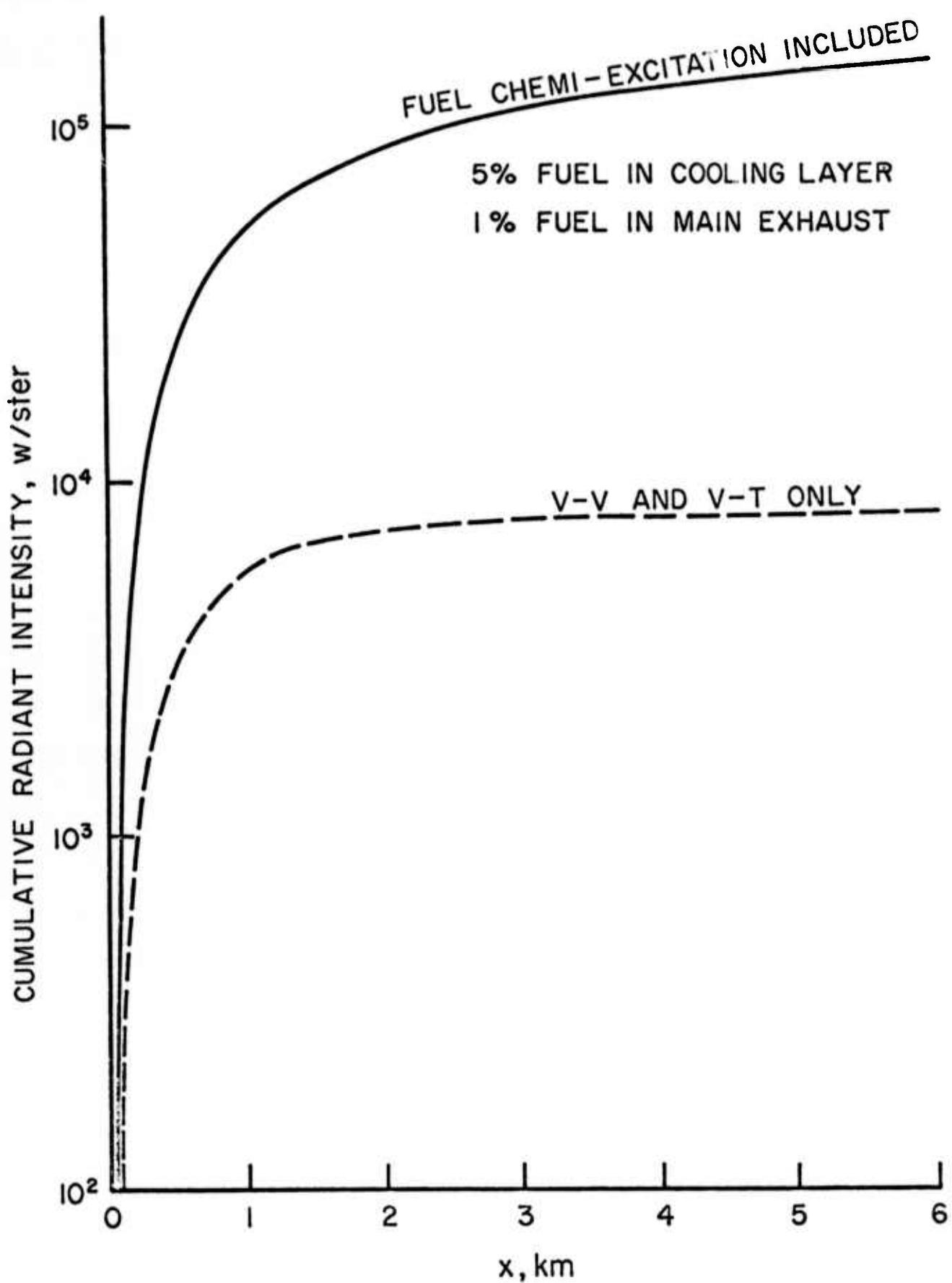


FIGURE 4. The effect of chemi-excitation on predicted cumulative radiant intensity.

- 2) The photon yields may be optimistic, although a rather drastic decrease would still allow substantial chemi-excitation relative to VT and VV excitation.
- 3) Unburned fuel could be ejected from the engine or turbine exhaust in the form of droplets which would have to be vaporized in the plume before reacting.  
[Webber, et al (1972), using a detailed combustion code to evaluate the external surface contamination potential due to unburned propellants from two small engines, indicates that essentially all unburned propellant leaving these engines is in the form of small droplets.]

However, even with these qualifications, it is evident that there is a distinct possibility that external chemiluminescence of unburned fuel species comprises a substantial fraction of amine-fueled missile plume signatures. This possibility should not be ignored in studies aimed at elucidating plume emission mechanisms.

## SUMMARY

The availability of baseline chemistry models for four rocket plume environments has been established. The mechanism for determining the important relaxation processes in systems involving non-equilibrium distributions of N<sub>2</sub>, H<sub>2</sub>, CO, O, H, H<sub>2</sub>O and CO<sub>2</sub> has been presented and preliminary calculations shown. An amine/substituted hydrazine model has been detailed and calculations appropriate to the TITAN mixing layer presented. As was found in the case of hydrocarbon afterburning in the ATLAS vehicle [Fisher (1973c)], minor quantities of unreacted amine or hydrazine in the plume flow can lead to a significant amount of plume radiation in the IR.

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APPENDIX I  
BASELINE CHEMISTRY MODELS

- |                         |    |
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| (1) APOLLO Model        | 34 |
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## (1) APOLLO MODEL

<u>Reaction</u>	<u>Reference</u>	<u>Rate Constant (cc/molecule-sec)</u>
1) O + H <sub>2</sub> → OH + H	(a,b)	1.65 <sup>-13</sup> exp(-2500/T)
2) H + OH → O + H <sub>2</sub>	(c)	6.9 <sup>-14</sup> exp(-1425/T)
3) O + H <sub>2</sub> (v=1) → OH + H	(d)	1.3 <sup>-10</sup> α (α = 0.9, 0.5)
4) H + OH → O + H <sub>2</sub> (v=1)	(c)	5.5 <sup>-11</sup> α exp(-4925/T)
5) O + H <sub>2</sub> (v=1) → OH(v=1) + H	(d)	1.3 <sup>-10</sup> (1 - α)
6) H + OH(v=1) → O + H <sub>2</sub> (v=1)	(c)	5.5 <sup>-11</sup> (1 - α) exp(215/T)
7) OH + H <sub>2</sub> → H <sub>2</sub> O + H	(d)	3.8 <sup>-11</sup> exp(-2600/T)
8) H + H <sub>2</sub> O → OH + H <sub>2</sub>	(c)	1.5 <sup>-10</sup> exp(-10075/T)
9) OH + H <sub>2</sub> (v=1) → H <sub>2</sub> O + H	(e)	1.5 <sup>-10</sup>
10) H + H <sub>2</sub> O → OH + H <sub>2</sub> (v=1)	(c)	5.8 <sup>-10</sup> exp(-13475/T)
11) OH(v=1) + H <sub>2</sub> → H <sub>2</sub> O + H	(e)	1.5 <sup>-11</sup>
12) H + H <sub>2</sub> O → OH(v=1) + H <sub>2</sub>	(c)	5.8 <sup>-11</sup> exp(-12475/T)
13) OH + OH → H <sub>2</sub> O + O	(a)	9.6 <sup>-12</sup> exp(-390/T)
14) O + H <sub>2</sub> O → OH + OH	(a)	9.5 <sup>-11</sup> exp(-9000/T)
15) O + OH → O <sub>2</sub> + H	(f)	4 <sup>-11</sup>
16) H + O <sub>2</sub> → O + OH	(c)	6.9 <sup>-10</sup> exp(-8400/T)
17) O + OH(v=1) → O <sub>2</sub> + H	(f)	4 <sup>-11</sup>
18) H + O <sub>2</sub> → O + OH(v=1)	(c)	6.9 <sup>-10</sup> exp(-13400/T)

## ENERGY TRANSFER REACTIONS\*

### Vibration-Translation Processes:

19) $H_2(v=1) + H \rightarrow H_2 + H$	(g)	$3.2^{-11} \exp(-1400/T)$
20) $H_2(v=1) + O \rightarrow H_2 + O$	(e)	$3.0^{-13} \sqrt{T}$
21) $H_2(v=1) + H_2 \rightarrow H_2 + H_2$	(h,i)	$1.5^{-7} \exp(-139/T^{1/3})$
22) $H_2(v=1) + H_2O \rightarrow H_2 + H_2O$	(e,j)	$1.5^{-7} \exp(-139/T^{1/3})$
23) $N_2(v=1) + H \rightarrow N_2 + H$	(u)	$1.9^{-6} \exp(-164/T^{1/3})$
24) $N_2(v=1) + O \rightarrow N_2 + O$	(k,l,m)	$1.2^{-13} \exp(-23/T^{1/3})$
25) $N_2(v=1) + H_2 \rightarrow N_2 + H_2$	(n)	$3.9^{-8} \exp(-164/T^{1/3})$
26) $N_2(v=1) + H_2O \rightarrow N_2 + H_2O$	(e,j)	$3.9^{-8} \exp(-164/T^{1/3})$
27) $OH(v=1) + H \rightarrow OH + H$	(e)	$3^{-11}$
28) $OH(v=1) + O \rightarrow OH + O$	(e)	$3^{-11}$
29) $OH(v=1) + H_2 \rightarrow OH + H_2$	(e)	$1^{-11}$
30) $OH(v=1) + H_2O \rightarrow OH + H_2O$	(e)	$3^{-12}$
31) $H_2O(010) + H \rightarrow H_2O(000) + H$	(e)	$1^{-11}$
32) $H_2O(010) + O \rightarrow H_2O(000) + O$	(e)	$1^{-11}$
33) $H_2O(010) + H_2 \rightarrow H_2O(000) + H_2$	(e,o)	$1^{-11}$
34) $H_2O(010) + H_2O \rightarrow H_2O(000) + H_2O$	(p)	$1^{-11}$
35) $H_2O(020) + H \rightarrow H_2O(010) + H$	(t)	$2^{-11}$
36) $H_2O(020) + O \rightarrow H_2O(010) + O$	(t)	$2^{-11}$
37) $H_2O(020) + H_2 \rightarrow H_2O(010) + H_2$	(t)	$2^{-11}$
38) $H_2O(020) + H_2O \rightarrow H_2O(010) + H_2O$	(t)	$2^{-11}$

---

\* Note that the reverse rate coefficient can be calculated directly from detailed balance.

39)	$H_2O(001) + H \rightarrow H_2O(000) + H$	(e)	$1^{-11}$
40)	$H_2O(001) + O \rightarrow H_2O(000) + O$	(e)	$1^{-11}$
41)	$H_2O(001) + H_2 \rightarrow H_2O(000) + H_2$	(o)	$2^{-13}$
42)	$H_2O(001) + H_2O \rightarrow H_2O(000) + H_2O$	(q)	$1^{-12}$
43)	$H_2O(001) + H \rightarrow H_2O(020) + H$	(e)	$1^{-11}$
44)	$H_2O(001) + O \rightarrow H_2O(020) + O$	(e)	$1^{-11}$
45)	$H_2O(001) + H_2 \rightarrow H_2O(020) + H_2$	(e)	$1^{-11}$
46)	$H_2O(001) + H_2O \rightarrow H_2O(020) + H_2O$	(e)	$1^{-11}$

#### Vibration-Vibration Processes

47)	$H_2(v=1) + H_2O(000)$ $\rightarrow H_2(v=0) + H_2O(001)$	(r)	$2.5^{-14} T^{5/6} \exp(-30.1/T^{1/3})$
48)	$H_2(v=1) + OH(v=0)$ $\rightarrow H_2(v=0) + OH(v=1)$	(e)	$1^{-12}$
49)	$N_2(v=1) + H_2O(010)$ $\rightarrow N_2(v=0) + H_2O(001)$	(e)	$3^{-13}$
50)	$N_2(v=1) + H_2O(000)$ $\rightarrow N_2(v=0) + H_2O(010)$	(s)	$9.4^{-11} \exp(-64/T^{1/3})$
51)	$H_2O(010) + H_2O(010)$ $\rightarrow H_2O(020) + H_2O(000)$	(e)	$1^{-12} \sqrt{T}$
52)	$H_2O(001)$ and $H_2O(100)$ assumed in quasi-equilibrium at the local translational temperature.		

References (Apollo Model)

- a) D.L. Baulch, et. al., High Temperature Reaction Rate Data, Leeds University, (1969).
- b) F.P. Boynton, Semi Annual Technical Report No. 1, Physical Dynamics Report PD-72-020, February(1972).
- c) calculated from the forward rate coefficient and detailed balance, using the equilibrium constant as given in the Leeds review [(a) above].
- d) estimated from the Leeds review [(a) above] using a method outlined in (b) above.
- e) estimate
- f) W.E. Wilson Jr., J. Phys. Chem. Refer. Data 1, 535 (1972).
- g) R.F. Hiedner and V.V. Casper, Chem. Phys. Letters 15, 179(1972)
- h) J.H. Kieffer and R.W. Lutz, J. Chem. Phys. 44, 658(1966) 45, 3888(1966).
- i) C. Joffrin, J. Ducuing and J.P. Coffinet, Opt. Commun. 2, 245(1970).
- j) past measurements involving water presumably measure both VV and VT processes.
- k) W.D. Breshears and P.F. Bird, J. Chem. Phys. 48, 4768 (1968).
- l) R.J. McNeal, M.E. Whitson Jr. and G.R. Cook, preprint of work submitted to Chem. Phys. Letters(1972). Aerospace Report SPL 3303, July(1972).
- m) D.J. Eckstrom, Stanford Research Institute, unpublished results.
- n) D.R. White, J. Chem. Phys. 46, 2016(1967).
- o) estimate based on Marriott's cross section values see E.R. Fisher, AFCRL Special Report, 72-0539, August(1972).
- p) estimate based on all available data
- q) estimate based on analogy to HF VT relaxation

- r) estimate based on the modified Rapp model, J. Chem. Phys. 40, 573(1964); Fisher unpublished results.
- s) estimate based on data of C.W. Von Rosenberg, K.N.C. Bray and N.H. Pratt, J. Chem. Phys. 56, 3230(1972) and 13th Symp. (Intern.) on combustion p. 89, (1971).
- t) scaled from the analogous rate constant for exciting the lowest bending mode.
- u) estimated based on the rate for CO + H; see reference (o) under RELAXATION MODEL (2).

(2) RELAXATION MODEL

<u>Vibration-Translation Processes</u>	<u>Reference</u>	<u>Rate Constant (cc/molecule-sec)</u>
1) $H_2(v=1) + H \rightarrow H_2 + H$	(a)	$3.2^{-11} \exp(-1400/T)$
2) $H_2(v=1) + O \rightarrow H_2 + O$	(b)	$3.0^{-13} \sqrt{T}$
3) $H_2(v=1) + H_2 \rightarrow H_2 + H_2$	(c,d)	$1.5^{-7} \exp(-139/T^{1/3})$
4) $H_2(v=1) + H_2O \rightarrow H_2 + H_2O$	(b,e)	$1.5^{-7} \exp(-139/T^{1/3})$
5) $N_2(v=1) + H \rightarrow N_2 + H$	(y)	$1.9^{-6} \exp(-164/T^{1/3})$
6) $N_2(v=1) + O \rightarrow N_2 + O$	(f,g,h)	$1.2^{-13} \exp(-23/T^{1/3})$
7) $N_2(v=1) + H_2 \rightarrow N_2 + H_2$	(i)	$3.9^{-8} \exp(-164/T^{1/3})$
8) $N_2(v=1) + H_2O \rightarrow N_2 + H_2O$	(b,e)	$3.9^{-8} \exp(-164/T^{1/3})$
9) $OH(v=1) + H \rightarrow OH + H$	(b)	$3^{-11}$
10) $OH(v=1) + O \rightarrow OH + O$	(b)	$3^{-11}$
11) $OH(v=1) + H_2 \rightarrow OH + H_2$	(b)	$1^{-11}$
12) $OH(v=1) + H_2O \rightarrow OH + H_2O$	(b)	$3^{-12}$
13) $H_2O(010) + H \rightarrow H_2O(000) + H$	(b)	$1^{-11}$
14) $H_2O(010) + O \rightarrow H_2O(000) + O$	(b)	$1^{-11}$
15) $H_2O(010) + H_2 \rightarrow H_2O(000) + H_2$	(b,j)	$1^{-11}$
16) $H_2O(010) + H_2O \rightarrow H_2O(000) + H_2O$	(k)	$1^{-11}$
17) $H_2O(001) + H \rightarrow H_2O(000) + H$	(b)	$1^{-11}$
18) $H_2O(001) + O \rightarrow H_2O(000) + O$	(b)	$1^{-11}$
19) $H_2O(001) + H_2 \rightarrow H_2O(000) + H_2$	(j)	$2^{-13}$
20) $H_2O(001) + H_2O \rightarrow H_2O(000) + H_2O$	(l)	$1^{-12}$

21)	$H_2O(001) + H \rightarrow H_2O(020) + H$	(b)	$1^{-11}$
22)	$H_2O(001) + O \rightarrow H_2O(020) + O$	(b)	$1^{-11}$
23)	$H_2O(001) + H_2 \rightarrow H_2O(020) + H_2$	(b)	$1^{-11}$
24)	$H_2O(001) + H_2O \rightarrow H_2O(020) + H_2O$	(b)	$1^{-11}$
25)	$CO(v=1) + H \rightarrow CO(v=0) + H$	(o)	$5.3^{-7} \exp(-119/T^{1/3})$
26)	$CO(v=1) + O \rightarrow CO(v=0) + O$	(p)	$1^{-8} \exp(-96/T^{1/3})$
27)	$CO(v=1) + H_2 \rightarrow CO(v=0) + H_2$	(q)	$9^{-9} \exp(-119/T^{1/3})$
28)	$CO(v=1) + H_2O \rightarrow CO(v=0) + H_2O$	(b)	$9^{-9} \exp(-119/T^{1/3})$
29)	$CO_2(010) + H \rightarrow CO_2(000) + H$	(b)	$3.8^{-12} \exp(-7/T^{1/3})$
30)	$CO_2(010) + O \rightarrow CO_2(000) + O$	(p)	$2.3^{-9} \exp(-77/T^{1/3})$
31)	$CO_2(010) + H_2 \rightarrow CO_2(000) + H_2$	(r)	$7.6^{-12} \exp(-7/T^{1/3})$
32)	$CO_2(010) + H_2O \rightarrow CO_2(000) + H_2O$	(s)	$1^{-11}$
33)	$CO_2(010) + CO_2 \rightarrow CO_2(000) + CO_2$	(r)	$4.6^{-10} \exp(-77/T^{1/3})$
34)	$CO_2(001) + H \rightarrow CO_2(000) + H$	(t)	$6.7^{-8} \exp(-208/T^{1/3})$
35)	$CO_2(001) + O \rightarrow CO_2(000) + O$	(t)	$1^{-8} \exp(-96/T^{1/3})$
36)	$CO_2(001) + H_2 \rightarrow CO_2(000) + H_2$	(t)	$9^{-9} \exp(-119/T^{1/3})$
37)	$CO_2(001) + H_2O \rightarrow CO_2(000) + H_2O$	(t)	$9^{-9} \exp(-119/T^{1/3})$
38)	$CO_2(001) + H \rightarrow CO_2(030) + H$	(b)	$2.13^{17} T^{-6.34} \exp(-3013/T - 378.7/T^{1/3} + 1416/T^{2/3})$
39)	$CO_2(001) + O \rightarrow CO_2(030) + O$	(u)	$4.6^{24} T^{-5.89} \exp(-4223/T - 672.7/T^{1/3} + 2683/T^{2/3})$
40)	$CO_2(001) + H_2 \rightarrow CO_2(030) + H_2$	(v)	$4.27^{17} T^{-6.34} \exp(-3013/T - 378.7/T^{1/3} + 1416/T^{2/3})$

41)	$\text{CO}_2(001) + \text{H}_2\text{O} \rightarrow \text{CO}_2(030) + \text{H}_2\text{O}$	(v)	$4.71^{-40} T^{4.54} \exp(2081/T)$ $+ 454/T^{1/3} - 1729/T^{2/3})$
42)	$\text{CO}_2(001) + \text{CO}_2 \rightarrow \text{CO}_2(030) + \text{CO}_2$	(v)	$9.16^{23} T^{-5.89} \exp(-4223/T)$ $- 672.7/T^{1/3} + 2683/T^{2/3})$
43)	$\text{CO}_2(001) + \text{CO} \rightarrow \text{CO}_2(030) + \text{CO}$	(v)	$6.87^{23} T^{-5.89} \exp(-4223/T)$ $- 672.7/T^{1/3} + 2683/T^{2/3})$
44)	$\text{CO}_2(001) + \text{N}_2 \rightarrow \text{CO}_2(030) + \text{N}_2$	(v)	$6.87^{23} T^{-5.89} \exp(-4223/T)$ $- 672.7/T^{1/3} + 2683/T^{2/3})$

### Vibration-Vibration Processes

45)	$\text{H}_2(v=1) + \text{H}_2\text{O}(000)$ $\rightarrow \text{H}_2(v=0) + \text{H}_2\text{O}(001)$	(m)	$2.5^{-14} T^{5/6} \exp(-30.1/T^{1/3})$
46)	$\text{H}_2(v=1) + \text{OH}(v=0)$ $\rightarrow \text{H}_2(v=0) + \text{OH}(v=1)$	(b)	$1^{-12}$
47)	$\text{N}_2(v=1) + \text{H}_2\text{O}(010)$ $\rightarrow \text{N}_2(v=0) + \text{H}_2\text{O}(001)$	(b)	$3^{-13}$
48)	$\text{N}_2(v=1) + \text{H}_2\text{O}(000)$ $\rightarrow \text{N}_2(v=0) + \text{H}_2\text{O}(010)$	(n)	$9.4^{-11} \exp(-64/T^{1/3})$
49)	$\text{H}_2\text{O}(010) + \text{H}_2\text{O}(010)$ $\rightarrow \text{H}_2\text{O}(020) + \text{H}_2\text{O}(000)$	(b)	$1^{-12} \sqrt{T}$
50)	$\text{CO}_2(001) + \text{H}_2\text{O}(000)$ $\rightarrow \text{CO}_2(010) + \text{H}_2\text{O}(010)$	(b)	$1^{-13}$

- 51)  $N_2(v=1) + CO_2(000)$   
 $\rightarrow N_2(v=0) + CO_2(001)$  (r) Take the largest value  $\begin{cases} 1.71^{-6} \exp(-175.3/T^{1/3}) \\ 6.07^{-14} \exp(15.3/T^{1/3}) \end{cases}$
- 52)  $N_2(v=1) + CO(v=0)$   
 $\rightarrow N_2(v=0) + CO(v=1)$  (v) Take the largest value  $\begin{cases} 1.78^{-6} \exp(-210/T^{1/3}) \\ 6.98^{-13} \exp(-25.6/T^{1/3}) \end{cases}$
- 53)  $CO_2(001) + CO(v=0)$   
 $\rightarrow CO_2(000) + CO(v=1)$  (b)  $1.56^{-11} \exp(-30.1/T^{1/3})$
- 54)  $CO_2(101) + H_2O(000)$   
 $\rightarrow CO_2(000) + H_2O(001)$  (b)  $2^{-13} \sqrt{T}$
- 55)  $CO_2(021) + H_2O(000)$   
 $\rightarrow CO_2(000) + H_2O(001)$  (b)  $2^{-13} \sqrt{T}$
- 56)  $CO_2(101) + CO_2(000)$   
 $\rightarrow CO_2(100) + CO_2(001)$  (b)  $2^{-11} \sqrt{T}$
- 57)  $CO_2(020) + CO_2(000)$   
 $\rightarrow CO_2(010) + CO_2(010)$  (b)  $4^{-13} \sqrt{T}$
- 58)  $H_2O(020) + H \rightarrow H_2O(010) + H$  (w)  $2^{-11}$
- 59)  $H_2O(020) + O \rightarrow H_2O(010) + O$  (w)  $2^{-11}$
- 60)  $H_2O(020) + H_2 \rightarrow H_2O(010) + H_2$  (w)  $2^{-11}$
- 61)  $H_2O(020) + H_2O \rightarrow H_2O(010) + H_2O$  (w)  $2^{-11}$
- 62)  $CO_2(020) + H \rightarrow CO_2(010) + H$  (w)  $7.6^{-12} \exp(-7/T^{1/3})$
- 63)  $CO_2(020) + O \rightarrow CO_2(010) + O$  (w)  $4.6^{-9} \exp(-77/T^{1/3})$
- 64)  $CO_2(020) + H_2 \rightarrow CO_2(010) + H_2$  (w)  $1.5^{-11} \exp(-7/T^{1/3})$
- 65)  $CO_2(020) + H_2O \rightarrow CO_2(010) + H_2O$  (w)  $2^{-11}$

- 66)  $\text{CO}_2(020) + \text{CO}_2 \rightarrow \text{CO}_2(010) + \text{CO}_2$  (w)  $9.2^{-10} \exp(-77/T^{1/3})$   
67)  $\text{CO}_2(030) + \text{H} \rightarrow \text{CO}_2(020) + \text{H}$  (w)  $1.2^{-11} \exp(-7/T^{1/3})$   
68)  $\text{CO}_2(030) + \text{O} \rightarrow \text{CO}_2(020) + \text{O}$  (w)  $6.9^{-9} \exp(-77/T^{1/3})$   
69)  $\text{CO}_2(030) + \text{H}_2 \rightarrow \text{CO}_2(020) + \text{H}_2$  (w)  $2.3^{-11} \exp(-7/T^{1/3})$   
70)  $\text{CO}_2(030) + \text{H}_2\text{O} \rightarrow \text{CO}_2(020) + \text{H}_2\text{O}$  (w)  $3^{-11}$   
71)  $\text{CO}_2(030) + \text{CO}_2 \rightarrow \text{CO}_2(020) + \text{CO}_2$  (w)  $1.4^{-9} \exp(-77/T^{1/3})$   
72)  $\text{H}_2\text{O}(100)$  and  $\text{H}_2\text{O}(001)$  assumed in quasi-equilibrium at the local translational temeprature.  
73)  $\text{CO}_2(100) + \text{M} \rightarrow \text{CO}_2(020) + \text{M}$  (x)  $1^{-10}$

### References (Vibrational Relaxation Model)

- (a) R.F. Hiedner and V.V. Casper, Chem. Phys. letters 15, 179(1972).
- (b) estimate
- (c) J.H. Kieffer and R.W. Lutz, J. Chem. Phys. 44, 658 (1966); 45, 3888(1966).
- (d) C. Joffrin, J. Ducuing and J.P. Coffinet, Opt, Commun. 2, 245(1970).
- (e) past measurements involving water presumably measure both VV and VT processes.
- (f) W.D. Breshears and P.F. Bird, J. Chem. Phys. 48, 4768 (1968).
- (g) R.J. McNeal, M.E. Whitson Jr. and G.R. Cook, preprint of work submitted to Chem. Phys. Letters (1972). Aerospace Report SPL 3303, July(1972).
- (h) D.J. Eckstrom, Stanford Research Institute, unpublished results.
- (i) D.R. White, J. Chem. Phys. 46, 2016(1967).
- (j) estimate based on Marriott's cross section values see E.R. Fisher, AFCRL Special Report, 72-0539, August (1972).
- (k) estimate based on all available data
- (l) estimate based on analogy to HF VT relaxation
- (m) estimate based on the modified Rapp model, J. Chem. Phys. 40, 573(1964) Fisher unpublished results.
- (n) estimate based on data of C.W. Von Rosenberg, K.N.C. Bray and N.H. Pratt, J. Chem. Phys. 56, 3230(1972) and 13th Symp. (Intern.) on combustion p. 89, (1971).
- (o) C.N. Rosenberg, R. Taylor and D. Teare, J. Chem. Phys. 54, 1974(1971). Also assuming the  $\text{CO}_2 + \text{H}_2$  activation energy, as shown in reaction 27).
- (p) unpublished data from AVCO.

- (q) W. J. Hocher and R. C. Millikan, J. Chem. Phys. 38, 214 (1963); and R. C. Millikan, J. Chem. Phys. 38, 2855 (1963).
- (r) R. Taylor and S. Bitterman, Rev. Mod. Phys. 41, 26 (1969).
- (s) M.I. Buckwald and S. H. Bauer, J. Phys. Chem. 76, 3108 (1972).
- (t) since direct VT relaxation of  $\text{CO}_2(v_3)$  to ground state has not been unambiguously determined without competing VV processes,  $\text{CO}_2(v_3)$  was assumed to relax like  $\text{CO}(v=1)$ .
- (u) estimate based on analogy with reaction 35).
- (v) estimate based on AVCO suggestion.
- (w) scaled from the analogous rate constant for exciting the lowest bending mode.
- (x) the Fermi resonance in  $\text{CO}_2$  is assumed to couple the (100) and (020) modes with a gas kinetic efficiency independent of collision partner.
- (y) estimated based on the rate for  $\text{CO} + \text{H}$ , under (o) above.

## (3) HYDROCARBON MODEL

LUMPED PARAMETER  
IR REACTION SCHEME

<u>Reaction</u>	<u>Rate Constant, cc/sec</u>	<u>Photon Yield</u>
1. A + O → R + OH	$1.3 \times 10^{-10} e^{-4840/RT}$	--
2. A + OH → R + H <sub>2</sub> O	$1.2 \times 10^{-11} e^{-850/RT}$	1
3. R + O → O $\cdot$ + OH	$1 \times 10^{-11}$	6
4. R + OH → O $\cdot$ + H <sub>2</sub> O	$1 \times 10^{-11}$	7
5. O $\cdot$ + O → (80%) R + CHO + (20%) C <sub>2</sub> H <sub>5</sub> + CHO	$1 \times 10^{-11}$	--
6. C <sub>2</sub> H <sub>6</sub> + OH → C <sub>2</sub> H <sub>5</sub> + H <sub>2</sub> O	$1.8 \times 10^{-11} e^{-2480/RT}$	1
7. C <sub>2</sub> H <sub>5</sub> + O → C <sub>2</sub> H <sub>4</sub> + OH	$1 \times 10^{-11}$	5
8. C <sub>2</sub> H <sub>5</sub> + OH → C <sub>2</sub> H <sub>4</sub> + H <sub>2</sub> O	$1 \times 10^{-11}$	5
9. C <sub>2</sub> H <sub>4</sub> + O → CH <sub>3</sub> + CHO	$5 \times 10^{-12} e^{-1040/RT}$	--
10. C <sub>2</sub> H <sub>4</sub> + OH → CH <sub>3</sub> + CH <sub>2</sub> O	$1 \times 10^{-11} e^{+900/RT}$	--
11. CH <sub>4</sub> + OH → CH <sub>3</sub> + H <sub>2</sub> O	$4.0 \times 10^{-12} e^{-5000/RT}$	1
12. CH <sub>3</sub> + O <sub>2</sub> → CH <sub>2</sub> O + OH	$1.7 \times 10^{-13}$	1
13. CHO + O → CO + OH	$5 \times 10^{-11}$	8
14. CH <sub>2</sub> O + OH → CHO + H <sub>2</sub> O	$4 \times 10^{-14} e^{-1000/RT}$	2
15. CH <sub>2</sub> O + O → CHO + OH	$1 \times 10^{-12} e^{-1000/RT}$	1
16. CHO + OH → CO + H <sub>2</sub> O	$1 \times 10^{-12}$	9
17. OH + O → O <sub>2</sub> + H	$2.2 \times 10^{-11}$	--

## (3) HYDROCARBON MODEL

(cont'd)

18.	$\text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H}$	$9.3 \times 10^{-13} e^{-1080/RT}$	--
19.	$\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$	$3.7 \times 10^{-11} e^{-5150/RT}$	1
20.	$\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}$	$9.5 \times 10^{-12} e^{-780/RT}$	1
21.	$\text{OH} + \text{H} \rightarrow \text{H}_2 + \text{O}$	$1.2 \times 10^{-11} e^{-7300/RT}$	--
22.	$\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$	$3.7 \times 10^{-10} e^{-16,800/RT}$	--
23.	$\text{H} + \text{CO}_2 \rightarrow \text{CO} + \text{OH}$	$9.3 \times 10^{-11} e^{-23,500/RT}$	--
24.	$\text{H} + \text{H}_2\text{O} \rightarrow \text{OH} + \text{H}_2$	$1.4 \times 10^{-9} e^{-20,100/RT}$	--
25.	$\text{O} + \text{H}_2\text{O} \rightarrow \text{OH} + \text{OH}$	$9.5 \times 10^{-11} e^{-18,000/RT}$	--
26.	$\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$	$2.9 \times 10^{-11} e^{-9450/RT}$	--
27.	$\text{CH}_3 + \text{O} \rightarrow \text{CH}_2\text{O} + \text{H}$	$3.3 \times 10^{-11}$	--
28.	$\text{CHO} + \text{H} \rightarrow \text{CO} + \text{H}_2$	$3.3 \times 10^{-11}$	--

"A" is a saturated hydrocarbon,  $\text{C}_n\text{H}_{2n+2}$ , with  $n \geq 3$

"R" is an alkyl radical,  $\text{C}_n\text{H}_{2n+1}$ , with  $n \geq 3$

"Ol" is an olefinic hydrocarbon,  $\text{C}_n\text{H}_{2n}$ , with  $n \geq 3$

## (4) AMINE MODEL

## INFRARED HYDRAZINE MODEL A

FUEL CHEMI-EXCITATION REACTIONS

<u>Reaction</u>	<u>Forward Rate Constant cc/sec</u>	<u>Reaction Energy kcal/gmole</u>
O + MMH → HN <sub>2</sub> CH <sub>3</sub> + H <sub>2</sub> O (001) (100) H <sub>2</sub> O (020) (010)	2 × 10 <sup>-11</sup>	-102
O + N <sub>2</sub> H <sub>4</sub> → N <sub>2</sub> H <sub>2</sub> + H <sub>2</sub> O (001) (100) H <sub>2</sub> O (020) (010)	1.8 × 10 <sup>-11</sup>	-90
O + UDMH → HN <sub>2</sub> (CH <sub>3</sub> ) <sub>2</sub> + OH	1 × 10 <sup>-12</sup>	-25
OH + N <sub>2</sub> H <sub>4</sub> → NH <sub>3</sub> + NH <sub>2</sub> O	2 × 10 <sup>-11</sup>	

## (4) AMINE MODEL

(cont'd)

REACTIONS OF OH AND H<sub>2</sub>O

<u>Reaction</u>	<u>Rate Constant cc/molecule-sec</u>
O + OH → O <sub>2</sub> + H	$4.0 \times 10^{-11}$
H <sub>2</sub> + O → +	$2.9 \times 10^{-11} e^{-4725/T}$
OH + H → H <sub>2</sub> + O	$1.22 \times 10^{-11} e^{-3650/T}$
H <sub>2</sub> * + O → OH + H	$0.65 \times 10^{-10}$
OH + H → H <sub>2</sub> * + O	$2.75 \times 10^{-11} e^{-4925/T}$
H <sub>2</sub> * + O → OH* + H	$0.65 \times 10^{-10}$
OH* + H → H <sub>2</sub> * + O	$2.75 \times 10^{-11} e^{215/T}$
OH + H <sub>2</sub> → H <sub>2</sub> O	$3.8 \times 10^{-11} e^{-2600/T}$
H <sub>2</sub> O + H → OH + H <sub>2</sub>	$1.5 \times 10^{-10} e^{-10075/T}$
OH + H <sub>2</sub> * → H <sub>2</sub> O* + H	$1.5 \times 10^{-10}$
H <sub>2</sub> O* + H → OH + H <sub>2</sub> *	$5.8 \times 10^{-10} e^{-13475/T}$
OH* + H → OH + H <sub>2</sub>	$1.5 \times 10^{-11}$
H <sub>2</sub> O* + H → OH* + H <sub>2</sub>	$5.8 \times 10^{-11} e^{-12475/T}$
OH + OH → H <sub>2</sub> O + O	$9.6 \times 10^{-12} e^{-390/T}$
H <sub>2</sub> O + O → OH + OH	$9.5 \times 10^{-11} e^{-9000/T}$
O + OH → O <sub>2</sub> + H	$4 \times 10^{-11}$
O <sub>2</sub> + H → OH + O	$6.9 \times 10^{-10} e^{-8400/T}$
O + OH* → O <sub>2</sub> + H	$4 \times 10^{-11}$
O <sub>2</sub> + H → O + OH*	$6.9 \times 10^{-10} e^{-13400/T}$

(4) AMINE MODEL  
(cont'd)

RELAXATION PROCESSES OF OH AND H<sub>2</sub>O

<u>Reaction</u>		<u>Forward Rate Constant (cc/molecule-sec)</u>
OH* + M ⇌ OH + M	M = H	$3 \times 10^{-11}$
"	M = O	$3 \times 10^{-11}$
"	M = H <sub>2</sub>	$1 \times 10^{-11}$
"	M = H <sub>2</sub> O	$3 \times 10^{-12}$
H <sub>2</sub> O(010) + M ⇌ H <sub>2</sub> O(000) + M	M = H	$2 \times 10^{-10}$
"	M = O	$1 \times 10^{-11}$
"	M = H <sub>2</sub>	$1 \times 10^{-11}$
"	M = H <sub>2</sub> O	$1 \times 10^{-11}$
H <sub>2</sub> O(100) + M ⇌ H <sub>2</sub> O + M	M = H	$1 \times 10^{-11}$
"	M = O	$1 \times 10^{-11}$
"	M = H <sub>2</sub>	$2 \times 10^{-13}$
"	M = H <sub>2</sub> O	$1 \times 10^{-12}$
H <sub>2</sub> O(001) + M ⇌ H <sub>2</sub> O + M	M = H	$1 \times 10^{-11}$
"	M = O	$1 \times 10^{-11}$
"	M = H <sub>2</sub>	$2 \times 10^{-13}$
"	M = H <sub>2</sub> O	$1 \times 10^{-12}$

## (4) AMINE MODEL

(cont'd)

$H_2O(001) + M \rightarrow H_2O(020) + M$	$M = H$	$1 \times 10^{-11}$
"	$M = O$	$1 \times 10^{-11}$
"	$M = H_2$	$1 \times 10^{-11}$
"	$M = H_2O$	$1 \times 10^{-11}$
$H_2O(100) + M \rightarrow H_2O(020) + M$	$M = H$	$1 \times 10^{-11}$
"	$M = O$	$1 \times 10^{-11}$
"	$M = H_2$	$1 \times 10^{-11}$
"	$M = H_2O$	$1 \times 10^{-11}$
$H_2O(010) + H_2O(010) \rightarrow H_2O(020) + H_2O$		$1 \times 10^{-12} \sqrt{T}$
$H_2O(020) + M \rightarrow H_2O(010) + M$	$M = H$	$2 \times 10^{-10}$
"	$M = O$	$1 \times 10^{-11}$
"	$M = H_2$	$1 \times 10^{-11}$
"	$M = H_2O$	$1 \times 10^{-11}$
$H + N_2H_4 \rightarrow N_2H_3 + H_2$		$2.2 \times 10^{-11} e^{-1260/T}$
$H + N_2H_3 \rightarrow 2NH_2$		
$H + N_2H_2 \rightarrow N_2H_3$		$1 \times 10^{-10}$
$O + NH_3 \rightarrow NH_2 + OH$		$2.5 \times 10^{-12} e^{-3000/T}$
$OH + NH_3 \rightarrow NH_2 + H_2O^{(*)}$		$6.6 \times 10^{-14} e^{-560/T} (T)^{.68}$

## (4) AMINE MODEL

(cont'd)

$O + NH_2 \rightarrow HNO + H$		$1 \times 10^{-11}$
$OH + HNO \rightarrow H_2O(*) + NO$		$3 \times 10^{-11}$
$H_2^* + M \rightarrow H_2 + M$	$M = H$	$3.2 \times 10^{-11} e^{-1400/T}$
"	$M = O$	$4.4 \times 10^{-13} \sqrt{T}$
"	$M = H_2$	$1.5 \times 10^{-7} e^{-139/T^{1/3}}$
"	$M = H_2O$	$1.5 \times 10^{-7} e^{-139/T^{1/3}}$
$N_2^* + M \rightarrow N_2 + M$	$M = H$	$6.7 \times 10^{-9} e^{-208/T^{1/3}}$
"	$M = O$	$1.2 \times 10^{-13} e^{-23/T^{1/3}}$
"	$M = H_2$	$3.9 \times 10^{-8} e^{-164/T^{1/3}}$
"	$M = H_2O$	$3.9 \times 10^{-8} e^{-164/T^{1/3}}$
$H_2^* + H_2O \rightarrow H_2 + H_2O(100)$		$2.5 \times 10^{-14} T^{5/6} e^{-30.1/T^{1/3}}$
$H_2^* + H_2\dot{O} \rightarrow H_2 + H_2O(001)$		$2.5 \times 10^{-14} T^{5/6} e^{-30.1/T^{1/3}}$
$H_2^* + OH \rightarrow H_2 + OH^*$		$1 \times 10^{-12}$
$N_2^* + H_2O(010) \rightarrow N_2 + H_2O(100)$		$3 \times 10^{-13}$
$N_2^* + H_2O(010) \rightarrow N_2 + H_2O(001)$		$3 \times 10^{-13}$
$N_2^* + H_2O \rightarrow N_2 + H_2O(010)$		$9.4 \times 10^{-11} e^{-64/T^{1/3}}$

## (4) AMINE MODEL

(cont'd)

$\text{CO}^* + \text{M} \rightarrow \text{CO} + \text{M}$	$\text{M} = \text{H}$	$6.7 \times 10^{-8} e^{-208/T^{1/3}}$
"	$\text{M} = \text{O}$	$1 \times 10^{-8} e^{-96/T^{1/3}}$
"	$\text{M} = \text{H}_2$	$9 \times 10^{-9} e^{-119/T^{1/3}}$
"	$\text{M} = \text{H}_2\text{O}$	$1 \times 10^{-8} e^{-96/T^{1/3}}$
$\text{CO}_2(010) + \text{M} \rightarrow \text{CO}_2 + \text{M}$	$\text{M} = \text{H}$	$3.8 \times 10^{-11} e^{-7/T^{1/3}}$
"	$\text{M} = \text{O}$	$2.3 \times 10^{-9} e^{-77/T^{1/3}}$
"	$\text{M} = \text{H}_2$	$7.6 \times 10^{-11} e^{-7/T^{1/3}}$
"	$\text{M} = \text{H}_2\text{O}$	$1 \times 10^{-11}$
"	$\text{M} = \text{CO}_2$	$4.6 \times 10^{-9} e^{-77/T^{1/3}}$
$\text{CO}_2(001) + \text{M} \rightarrow \text{CO}_2 + \text{M}$	$\text{M} = \text{H}$	$6.7 \times 10^{-8} e^{-208/T^{1/3}}$
"	$\text{M} = \text{O}$	$1 \times 10^{-8} e^{-96/T^{1/3}}$
"	$\text{M} = \text{H}_2$	$9 \times 10^{-9} e^{-119/T^{1/3}}$
"	$\text{M} = \text{H}_2\text{O}$	$9 \times 10^{-9} e^{-119/T^{1/3}}$

## (4) AMINE MODEL

(cont'd)

$\text{CO}_2(001) + \text{M} \rightarrow \text{CO}_2(030) + \text{M}$	$\text{M} = \text{H}$	$2.13 \times 10^{17} T^{-6.34} \exp(-3013/T)$ $- 378.7/T^{1/3} + 1416/T^{2/3}$
"	$\text{M} = \text{O}$	$4.6 \times 10^{24} T^{-5.89} \exp(-4223/T)$ $- 672.7/T^{1/3} + 2683/T^{2/3}$
"	$\text{M} = \text{H}_2$	$4.27 \times 10^{17} T^{-6.34} \exp(-3013/T)$ $- 378.7/T^{1/3} + 1416/T^{2/3}$
"	$\text{M} = \text{H}_2\text{O}$	$4.71 \times 10^{-40} T^{4.54} \exp(2081/T)$ $+ 454/T^{1/3} - 1729/T^{2/3}$
"	$\text{M} = \text{CO}_2$	$9.16 \times 10^{23} T^{-5.89} \exp(-4223/T)$ $- 672.7/T^{1/3} + 2683/T^{2/3}$
"	$\text{M} = \text{CO}$	$6.87 \times 10^{23} T^{-5.89} \exp(-4223/T)$ $- 672.7/T^{1/3} + 2683/T^{2/3}$
"	$\text{M} = \text{N}_2$	$6.87 \times 10^{23} T^{-5.89} \exp(-4223/T)$ $- 672.7/T^{1/3} + 2683/T^{2/3}$
$\text{CO}_2(001) + \text{H}_2\text{O} \rightarrow \text{CO}_2(010) + \text{H}_2\text{O}(010)$		$1 \times 10^{-13}$
$\text{N}_2^* + \text{CO}_2 \rightarrow \text{N}_2 + \text{CO}_2(001)$		$\left\{ \begin{array}{l} 1.72 \times 10^{-6} e^{-175/T^{1/3}} \\ 6 \times 10^{-14} e^{15.3/T^{1/3}} \end{array} \right\}$ largest

## (4) AMINE MODEL

(cont'd)

$N_2^* + CO \rightarrow N_2 + CO^*$		$\left\{ \begin{array}{l} 1.78 \times 10^{-6} e^{-210/T^{1/3}} \\ 7 \times 10^{-13} e^{-25.6/T^{1/3}} \end{array} \right\}$ largest
$CO_2(001) + CO \rightarrow CO_2 + CO^*$		$1.57 \times 10^{-11} e^{-30.1/T^{1/3}}$
$CO_2(101) + H_2O \rightarrow CO_2 + H_2O(100)$		$2 \times 10^{-13} \sqrt{T}$
$CO_2(101) + H_2O \rightarrow CO_2 + H_2O(001)$		$2 \times 10^{-13} \sqrt{T}$
$CO_2(021) + H_2O \rightarrow CO_2 + H_2O(100)$		$2 \times 10^{-13} \sqrt{T}$
$CO_2(021) + H_2O \rightarrow CO_2 + H_2O(001)$		$2 \times 10^{-13} \sqrt{T}$
$CO_2(101) + CO_2 \rightarrow CO_2(001) + CO_2(100)$		$2 \times 10^{-11} \sqrt{T}$
$CO_2(020) + CO_2 \rightarrow CO_2(010) + CO_2(010)$		$2 \times 10^{-13} \sqrt{T}$
$CO_2(100) + M \rightarrow CO_2 + M$	$M = H$	$3.8 \times 10^{-12} e^{-17.6/T^{1/3}}$
"	$M = O$	$2.3 \times 10^{-9} e^{-194/T^{1/3}}$
"	$M = H_2$	$7.6 \times 10^{-12} e^{-17.6/T^{1/3}}$
"	$M = H_2O$	$3 \times 10^{-13}$
$CO_2(101) + M \rightarrow CO_2(100) + M$	$M = H$	$6.7 \times 10^{-8} e^{-208/T^{1/3}}$
"	$M = O$	$1.0 \times 10^{-8} e^{-96/T^{1/3}}$
"	$M = H_2$	$9.0 \times 10^{-9} e^{-119/T^{1/3}}$
"	$M = H_2O$	$9.0 \times 10^{-9} e^{-119/T^{1/3}}$

## (4) AMINE MODEL

(cont'd)

$\text{CO}_2(101) + \text{M} \rightarrow \text{CO}_2(001) + \text{M}$	$\text{M} = \text{H}$	$3.8 \times 10^{-12} e^{-17.6/T^{1/3}}$
"	$\text{M} = \text{O}$	$2.3 \times 10^{-9} e^{-194/T^{1/3}}$
"	$\text{M} = \text{H}_2$	$4.6 \times 10^{-9} e^{-194/T^{1/3}}$
"	$\text{M} = \text{H}_2\text{O}$	$3 \times 10^{-13}$
$\text{CO}_2(020) + \text{M} \rightarrow \text{CO}_2(010) + \text{M}$	$\text{M} = \text{H}$	$3.8 \times 10^{-11} e^{-7/T^{1/3}}$
"	$\text{M} = \text{O}$	$2.3 \times 10^{-9} e^{-77/T^{1/3}}$
"	$\text{M} = \text{H}_2$	$7.6 \times 10^{-11} e^{-7/T^{1/3}}$
"	$\text{M} = \text{H}_2\text{O}$	$1.0 \times 10^{-11}$
"	$\text{M} = \text{CO}_2$	$4.6 \times 10^{-9} e^{-77/T^{1/3}}$
$\text{CO}_2(021) + \text{M} \rightarrow \text{CO}_2(011) + \text{M}$	$\text{M} = \text{H}$	$3.8 \times 10^{-11} e^{-7/T^{1/3}}$
"	$\text{M} = \text{O}$	$2.3 \times 10^{-9} e^{-77/T^{1/3}}$
"	$\text{M} = \text{H}_2$	$7.6 \times 10^{-11} e^{-7/T^{1/3}}$
"	$\text{M} = \text{H}_2\text{O}$	$1.0 \times 10^{-11}$
"	$\text{M} = \text{CO}_2$	$4.6 \times 10^{-9} e^{-77/T^{1/3}}$

## (4) AMINE MODEL

(cont'd)

$\text{CO}_2(011) + \text{M} \rightarrow \text{CO}_2(001) + \text{M}$	M = H	$3.8 \times 10^{-11} e^{-7/T^{1/3}}$
"	M = O	$2.3 \times 10^{-9} e^{-77/T^{1/3}}$
"	M = $\text{H}_2$	$7.6 \times 10^{-11} e^{-7/T^{1/3}}$
"	M = $\text{H}_2\text{O}$	$1.0 \times 10^{-11}$
"	M = $\text{CO}_2$	$4.6 \times 10^{-9} e^{-77/T^{1/3}}$
$\text{CO}_2(021) + \text{M} \rightarrow \text{CO}_2(020) + \text{M}$	M = H	$6.7 \times 10^{-8} e^{-208/T^{1/3}}$
"	M = O	$1.0 \times 10^{-8} e^{-96/T^{1/3}}$
"	M = $\text{H}_2$	$9.0 \times 10^{-9} e^{-119/T^{1/3}}$
"	M = $\text{H}_2\text{O}$	$9.0 \times 10^{-9} e^{-119/T^{1/3}}$
$\text{CO}_2(030) + \text{M} \rightarrow \text{CO}_2(020) + \text{M}$	M = H	$3.8 \times 10^{-11} e^{-7/T^{1/3}}$
"	M = O	$2.3 \times 10^{-9} e^{-77/T^{1/3}}$
"	M = $\text{H}_2$	$7.6 \times 10^{-11} e^{-7/T^{1/3}}$
"	M = $\text{H}_2\text{O}$	$1.0 \times 10^{-11}$

## (5) RADIATIVE LIFETIMES

<u>SPECIES</u>	<u>t(sec)</u>
OH(v=1)	0.3
H <sub>2</sub> O(100)	0.14
H <sub>2</sub> O(010)	0.045
H <sub>2</sub> O(001)	0.014
H <sub>2</sub> O(020)	0.022
CO <sub>2</sub> (010)	0.33
CO <sub>2</sub> (001)	0.0025
CO <sub>2</sub> (101)	0.091